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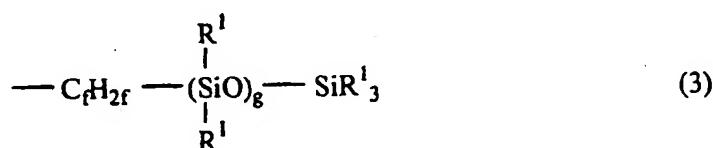
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(54) Cosmetic material

(57) A cosmetic material in which a silicone compound represented by the following formula (1) is mixed:



wherein R¹ groups, which are the same or different, each represent a hydrogen atom or an organic group selected from the class consisting of alkyl groups containing 1 to 30 carbon atoms, aryl groups, aralkyl groups, fluorinated alkyl groups and organic groups represented by the following formula (2); R² groups each represent a silicone group represented by the following formula (3); a is a number of from 1.0 to 2.5; b is a number of from 0.001 to 1.5;



wherein R³ is a hydrocarbon group containing 4 to 30 carbon atoms, or an organic group represented by R⁴-(CO)-; R⁴ is a hydrocarbon group containing 1 to 30 carbon atoms; c is an integer of from 0 to 15, d is an integer of from 0 to 50, and e is an integer of from 0 to 50; and f is an integer of from 1 to 5, and g is an integer of from 0 to 500. The silicone compounds represented by formula (1) not only have high compatibility with other ingredients of cosmetics, such as oils, surfactants and powders, to ensure high stability in the emulsified state, but also they produce an excellent effect in cleansing sebum stains and durable makeup stains.

EP 1 062 944 A1

Description**FIELD OF THE INVENTION**

5 [0001] The present invention relates to a cosmetic material which contains a specified silicone compound to acquire excellent emulsification suitability and high transparency, and besides, to ensure a feeling of refreshment for the users thereof. The present cosmetic material is usable for skin-care cosmetics, hair-care cosmetics, antiperspirant cosmetics, makeup cosmetics, UV protective cosmetics and so on.

BACKGROUND OF THE INVENTION

10 [0002] In general the makeup is smeared with secretion from humans, such as sweat, tear and sebum. In particular, the leading cause of the makeup spoilage consists in that the powder in a cosmetic material is wetted excessively by the sebum secreted from the skin in addition to oil ingredients compounded in the cosmetic material. Therefore, with the intention of reducing the oil ingredients remaining on the skin after the makeup is done, it has been attempted to use volatile oils, such as octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane, as a part of the oil ingredients compounded in a cosmetic material.

15 [0003] Further, the rub and the water given to the makeup constitute external factors inhibiting the makeup effect from lasting long. For the purpose of preventing the makeup from coming off by contact with aqueous substances, such as sweat and tears, or maintaining the skin protecting effect by preventing a loss of water-soluble components and sebum in the skin, it has been carried out to heighten the water repellency by mixing a silicone oil in the cosmetic material. In recent years, the silicone oils, represented, e.g., by dimethylpolysiloxanes, have been prevailingly used as an oil ingredient for cosmetic materials because of their characteristics, including light feel, excellent water repellency and high safety.

20 [0004] As mentioned above, dimethylpolysiloxanes possess excellent characteristics as an oil ingredient of cosmetic materials, but it cannot be said that the dimethylpolysiloxanes were successful in producing a satisfactory improvement on the water repellency of makeup cosmetics.

25 [0005] As to the skin care cosmetics also, there has been a demand for oil ingredients having a light feel, water repellency, good usability and a feel of cling to the skin.

30 [0006] On the other hand, the silicone oils produced by introducing fluoroalkyl groups into dimethylpolysiloxanes (Japanese Tokkai Hei 2-295912, wherein the term "Tokkai" means an "unexamined published patent application") have high water repellency, compared with dimethylpolysiloxanes. By increasing the content of fluoroalkyl groups therein, the silicone oils can have sufficiently high water repellency, but they come to have a heavy feel and lose solubilities in volatile oils, such as octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane; as a result, the usability thereof becomes poor. On the contrary, the fluoroalkyl content decreased in order to secure solubilities in volatile oils for the silicone oils can provide neither sufficient water repellency nor a feel of cling to the skin.

SUMMARY OF THE INVENTION

40 [0007] As a result of our intensive studies done aiming at developing a cosmetic material having a light feel, sufficiently high water repellency and a makeup effect of long-duration, it has been found that the one end reactive silicone-grafted silicone compounds have extremely high water repellency, solubilities in volatile oils, such as octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane, and good usability as oil ingredients of a cosmetic material, and besides, the cosmetic materials using them have a light feel, thereby achieving the present invention.

45 [0008] While the silicone compounds produced by the addition reaction of the foregoing silicone compounds to organohydrogenpolysiloxanes are disclosed in Japanese Tokkai Hei 7-197055 as actuation silicone oils having good low temperature characteristics, it is our finding that these silicone compounds are effective ingredients of cosmetic materials.

50 [0009] More specifically, when these silicone compounds are used as oils for emulsions, they can exhibit excellent ability to emulsify because of their excellent compatibility with oils used for general cosmetic materials, such as other silicone oils, ester oils and triglyceride. And the emulsions obtained can have satisfactory storage stability, so they are very effective for cosmetic use. Further, we have found that the aforementioned silicone compounds are instrumental in cleansing sebum stains and makeup stains from cosmetics of the type which are hard to come off, and the cleansing composition comprising them has a very good touch during and after cleansing treatment.

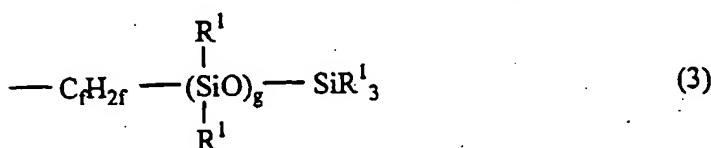
55 [0010] Therefore, an object of the invention is to provide a cosmetic material not only having high compatibility with other general cosmetic materials and ensuring high stability in the emulsions comprising them, thereby enabling the preparation of cosmetics having makeup effect of long duration, but also having excellent cleansing effect on both sebum stains and makeup stains of cosmetics of the type which are hard to come off, and that, ensuring a very good

touch during and after cleansing with cosmetics comprising them.

[0011] The above-described object is attained with a cosmetic material in which is mixed a silicone compound represented by the following formula (1):



wherein R¹ groups, which are the same or different, each represent a hydrogen atom or an organic group selected from the class consisting of alkyl groups containing 1 to 30 carbon atoms, aryl groups, aralkyl groups, fluorinated alkyl groups and organic groups represented by the following formula (2); R² groups each represent a silicone group represented by the following formula (3); a is a number of from 1.0 to 2.5; b is a number of from 0.001 to 1.5;



wherein R³ is a hydrocarbon group containing 4 to 30 carbon atoms or an organic group represented by R⁴-(CO)-; R⁴ is a hydrocarbon group containing 1 to 30 carbon atoms; c is an integer of from 0 to 15, d is an integer of from 0 to 50, and e is an integer of from 0 to 50; and f is an integer of from 1 to 5, and g is an integer of from 0 to 500.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The silicone compounds represented by formula $R_1^aR_2^bSiO(4-a-b)/2$ (herein referred to as formula (1)) are illustrated below in detail.

[0013] Each R¹ group represents an organic group selected from the class consisting of 1-30C alkyl groups, aryl groups, aralkyl groups, fluorinated alkyl groups and organic groups represented by $\text{C}_c\text{H}_{2c}\text{-O-(C}_2\text{H}_4\text{O)}_d(\text{C}_3\text{H}_6\text{O)}_e\text{R}^3$ (which is referred to as formula (2), wherein c, d and e are each an integer and fall within the following ranges: 0≤c≤15, 0≤d≤50, 0≤e≤50; and R³ represents a 4-30C hydrocarbon group or an organic group represented by R⁴ $\text{-}(\text{CO)-}$ wherein R⁴ represents a 1-30C hydrocarbon group).

[0014] Examples of an alkyl group as R₁ include a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group and a decyl group.

[0015] Examples of a cycloalkyl group as R¹ include a cyclopentyl group and a cyclohexyl group, those of an aryl group as R¹ include a phenyl group and a tolyl group, those of an aralkyl group as R¹ include a benzyl group and a

group as R¹ include a phenyl group and a vinyl group, and those of a phenyl group as R¹ include a trifluoropropyl group and a heptadecafluorodecyl group.

22-167 Examples of an organic group represented by formula (2) include higher alcohol residues, such as residues

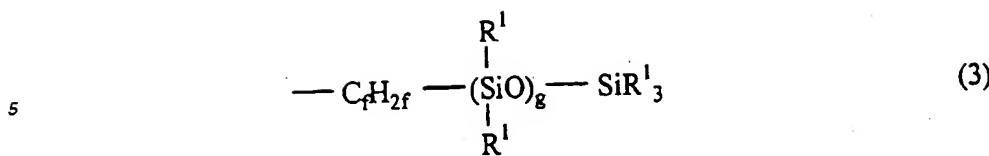
[0016] Examples of an organic group represented by formula (2) include higher alcohol residues, such as residues of higher alcohols, such as cetyl alcohol, oleyl alcohol and stearyl alcohol, and polyoxyalkylene adducts thereof; higher alcohol alkanyl ether residues, and polyoxyalkylene adducts thereof; higher fatty acid residues, such as residues of oleic acid, stearic acid and behenic acid, and polyoxyalkylene adducts thereof; and higher fatty acid alkanyl ester residues and polyoxyalkylene adducts thereof.

[0017] More specifically, the formula (2) is $-O-(C_2H_4O)_d(C_3H_6O)_eH^0$ when c is 0. Further, it becomes C_3H_6O in the case of e=0 and d=0, and represents a residue of higher alcohol such as cetyl alcohol, oleyl alcohol or stearyl alcohol, or a residue of higher fatty acid such as oleic acid, stearic acid or behenic acid. In a case of d,e ≥ 1 , on the other hand, the formula (2) represents an alcohol residue of higher alcohol/alkylene oxide adduct (having OH at the end).

[0018] When c is 1 or 2 the formula (2) is $-C_6H_{2c-2}O-(C_2H_4O)_d(C_3H_6O)_eR^3$, and this group is formed by dehydrohalogenation reaction between Si-OH group and $X(CH_2)_n-O-(C_2H_4O)_d(C_3H_6O)_eR^3$ (wherein X is halogen).

[0019] The $-C_cH_{2c}-O-(C_2H_4O)_d(C_3H_6O)_eR^3$ group in the case of $c \geq 3$ is a group introduced by the addition reaction between Si-H and a higher alcohol alkenyl ether or a fatty acid alkenyl ester (in a case of $d=e=0$), or a polyalkylene oxid adduct thereof (in a case of $d,e \geq 1$).

[0020] R² groups are each a silicon group represented by the following formula (3):

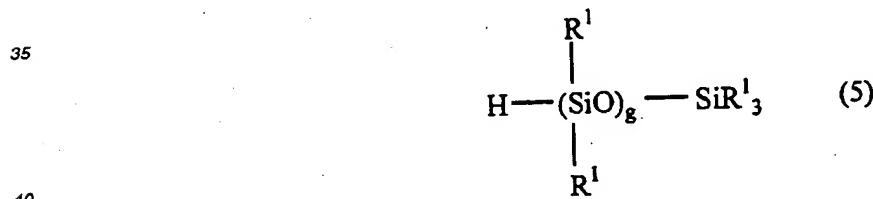
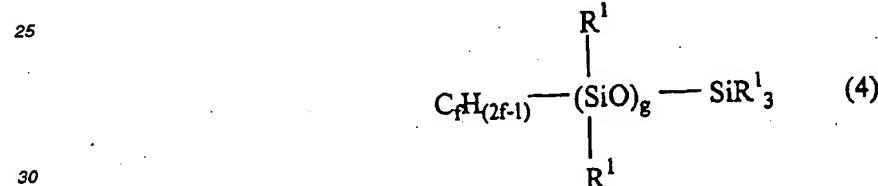


10 wherein f is an integer of from 1 to 5, and g is an integer of from 0 to 500, preferably from 3 to 100. For instance, f has a value of 2 when the silicone compound of formula (1) is synthesized by the reaction between a vinyl group and a SiH group. When the integer "g" in R² has a value greater than 500, such R² group is liable to have inferior reactivity in the introduction reaction into a compound constituting the main chain.

[0021] "a" in formula (1) is a number of from 1.0 to 2.5, preferably from 1.2 to 2.3, and "b" in formula (1) is a number of from 0.001 to 1.5, preferably from 0.05 to 1.0.

15 [0022] When the silicone compounds represented by formula (1) are used as oil ingredients of cosmetic material, the weight average molecular weight suitable therefor, though it has no particular limits, is from 500 to 200,000, preferably from 1,000 to 100,000.

20 [0023] The present silicone compounds represented by formula (1) can be synthesized with ease by addition reaction between organohydrogenpolysiloxanes and silicone compounds represented by the following general formula (4) and, if desired, olefin compounds as well in the presence of a platinum or rhodium catalyst, or by the reaction between silicone compounds represented by formula (5) and organovinylsiloxanes:



wherein R¹, f and g have the same meanings as in formula (3) respectively.

[0024] The organopolysiloxanes to constitute the main chains of the present silicone compounds may have a straight-chain structure or a cyclic structure. The suitable mixing ratio between a main chain polysiloxane and a silicone compound represented by formula (4) or (5) is from 0.5 to 2.0, preferably from 0.8 to 1.2, expressed in terms of the quantity by mole of the terminal unsaturated group per mole of SiH groups. The addition reaction is carried out effectively in the presence of a platinum catalyst or a rhodium catalyst. Suitable examples of such a catalyst include chloroplatinic acid, alcohol-modified chloroplatinic acid and chloroplatinic acid-vinylsiloxane complex.

50 [0025] The amount of catalyst used, though it may be a conventional catalytic amount, is desirably at most 500 ppm, particularly desirably at most 20 ppm, based on the platinum or the rhodium. The addition reaction may be carried out in an organic solvent, if needed. Examples of an organic solvent usable therein include aliphatic alcohols, such as methanol, ethanol, 2-propanol and butanol; aromatic hydrocarbons, such as toluene and xylene; aliphatic or alicyclic hydrocarbons, such as n-pentane, n-hexane and cyclohexane; and halogenated hydrocarbons, such as dichloromethane, chloroform and carbon tetrachloride. The addition reaction has no particular restriction as to its reaction conditions. However, it is desirable that the addition reaction be performed for 1 to 10 hours under reflux.

[0026] The present silicone compounds can be used for various purposes. In particular, they are suitable for materials of all cosmetics applied to skin and hair. The appropriate proportion of a silicone compound represented by formula

(1) mixed in such cosmetics each is from 0.1 to 80 % by weight.

[0027] The present cosmetic materials can further contain other oils depending on the desired purposes thereof. The oils used together may be in any of solid, semisolid and liquid states, provided that they have so far been used for general cosmetics.

5 [0028] More specifically, not only natural animal and vegetable fats and oils but also semi-synthetic fats and oils can be mixed in the present cosmetic material, with examples including avocado oil, linseed oil, almond oil, Chinese wax, perilla oil, olive oil, cacao butter, kapok wax, kaya oil, carnauba wax, liver oil, candellila wax, beef tallow, beef foot oil, 10 beef bone fat, hydrogenated beef tallow, apricot kernel oil, spermaceti, hydrogenated oil, wheat germ oil, sesame oil, rice germ oil, rice bran oil, sugar cane wax, sasanqua oil, safflower oil, shea butter, Chinese tung oil, cinnamon oil, jojoba wax, shellac wax, turtle oil, soybean oil, tea seed oil, tsubaki oil, evening primrose oil, corn oil, lard, rape seed oil, Japanese tung oil, rice-bran wax, germ oil, horse fat, persic oil, palm oil, palm kernel oil, castor oil, hydrogenated castor oil, methyl castor oil fatty acid, sunflower oil, grape seed oil, bayberry wax, jojoba oil, macadamia nut oil, beeswax, mink oil, cottonseed oil, cotton wax, Japan wax, haze kernel oil, montan wax, coconut oil, hydrogenated coconut oil, tricoconut oil fatty acid glyceride, mutton-tallow, peanut oil, lanolin, liquid lanolin, reduced lanolin, lanolin alcohol, hard lanolin, lanolin acetate, lanolin fatty acid isopropyl, hexyl laurate, POE lanolin alcohol ether, POE lanolin alcohol acetate, polyethylene glycol lanolin fatty acid, POE hydrogenated lanolin alcohol ether, and egg yolk oil.

15 [0029] Examples of hydrocarbon oil which can be mixed therein include ozokerite, squalane, squalene, ceresine, paraffin, paraffin wax, liquid paraffin, pristane, polyisobutylene, microcrystalline wax and Vaseline; and those of a higher fatty acid which can be mixed include lauric acid, myristic acid, palmitic acid, stearic acid, behenic acid, undecylenic acid, oleic acid, linoleic acid, linolenic acid, arachidonic acid, eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA), isostearic acid and 12-hydroxystearic acid.

20 [0030] Examples of a higher alcohol which can be mixed therein include lauryl alcohol, myristyl alcohol, palmityl alcohol, stearyl alcohol, behenyl alcohol, hexadecyl alcohol, oleyl alcohol, isostearyl alcohol, hexylundecanol, octyl-dodecanol, cetostearyl alcohol, 2-decyldodecyl palmitate, phytosterol, POE cholesterol ether, monostearyl glycerin ether (batyl alcohol) and monooleyl glyceryl ether (cerakyl alcohol).

25 [0031] Examples of ester oil which can be mixed therein include diisobutyl adipate, 2-hexyldecyl adipate, di-2-heptylundecyl adipate, N-alkylglycol monoisostearates, isocetyl isostearate, trimethylolpropane triisostearic acid ester, ethylene glycol di-2-ethylhexanoic acid ester, cetyl 2-ethylhexanoate, trimethylolpropane tri-2-ethylhexanoic acid ester, pentaerythritol tetra-2-ethylhexanoic acid ester, cetyl octanoate, octyldodecyl gum ester, oleyl oleate, octyldodecyl oleate, decyl oleate, neopentyl glycol dicapric acid ester, triethyl citrate, 2-ethylhexyl cinnamate, amyl acetate, ethyl acetate, butyl acetate, isocetyl stearate, butyl stearate, diisopropyl sebacate, di-2-ethylhexyl sebacate, cetyl lactate, myristyl lactate, isopropyl palmitate, 2-ethylhexyl palmitate, 2-hexyldecyl palmitate, 2-heptylundecyl palmitate, cholesteryl 12-hydroxystearate, dipentaerythritol fatty acid esters, isopropyl myristate, octyldodecyl myristate, 2-hexyldecyl myristate, myristyl myristate, hexyldecyl dimethylocanoate, ethyl laurate, hexyl laurate, N-lauroyl-L-glutaminic acid 2-octyldecyl ester and diisostearyl malic acid; and examples of glyceride oil which can be mixed therein include acetoglyceride, triisooctanoic acid glyceride, triisostearic acid glyceride, triisopalmitic acid glyceride, tri-2-ethylhexanoic acid glyceride, monostearic acid glyceride, di-2-heptylundecanoic acid glyceride, trimyristic acid glyceride and myristic acid isostearic acid diglyceride.

30 [0032] As examples of other silicone oils which can be mixed, mention may be made of organopolysiloxanes having from low to high viscosities, such as dimethylpolysiloxane, methylphenylpolysiloxane, methylhydrogenpolysiloxane, and dimethylsiloxane-methylphenylsiloxane copolymer; cyclic siloxanes, such as octamethylcyclotetrasiloxane, and decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, tetramethyltetrahydrogencyclotetrasiloxane; silicone rubbers, such as gummy dimethylpolysiloxanes having high polymerization degrees and gummy dimethylsiloxane-methylphenylsiloxane copolymers having high polymerization degrees; and cyclosiloxane solutions of silicone rubber, trimethylsiloxysilicate, cyclosiloxane solutions of trimethylsiloxysilicate, higher alkoxy-modified silicones such as stearoxysilicone, higher fatty acid-modified silicones, alkyl-modified silicones, amino-modified silicones, fluorine-modified silicones, and silicone resin solutions.

35 [0033] These silicone oils are not particularly restricted as to their structure, but they may have any of straight-chain, branched and cyclic structures. In particular, it is desirable that their main skeletons be $-\text{Si}-\text{O}-\text{Si}-$. Additionally, those silicone oils may have $-\text{Si}-(\text{CH}_2\text{CH}_2)_m-\text{Si}-$ linkage in part of their respective molecules.

40 [0034] As examples of fluorine-containing oil which can be mixed, mention may be made of perfluoropolyether, perfluorodecalin and perfluorooctane.

45 [0035] Furthermore, the present cosmetic material can contain one or more of a surfactant, if desired. The surfactant added thereto has no particular restriction, but it may be any of anionic, cationic, nonionic and amphoteric ones so long as they have hitherto been used in general cosmetics.

50 [0036] Examples of a usable anionic surfactant include fatty acid soap, such as sodium stearate or triethanolamine palmitate; alkyl ether carboxylic acids and salts thereof; salts of amino acid-fatty acid condensates; alkanesulfonates; alkenesulfonates; sulfonated fatty acid esters; sulfonates of formaldehyde condensate

type; alkylsulfates; higher secondary alcohol sulfates; alkyl and aryl ether sulfates; fatty acid ether sulfates, fatty acid alkylolamide sulfates; ether sulfates, such as Turkey red oil; alkyl phosphates; ether phosphates; alkyl aryl ether phosphates; amide phosphates; and activ agents of N-acylamino acid typ.

[0037] Examples of a usable cationic surfactant include amine salts, such as alkylammonium salts, polyamines and aminoalcohol fatty acid derivatives, quaternary alkylammonium salts, quaternary arylammonium salts, pyridinium salts and imidazolium salts.

[0038] Examples of a usable nonionic surfactant include sorbitan fatty acid esters, glycerin fatty acid esters, polyglycerin fatty acid esters, propylene glycol fatty acid esters, polyethylene glycol fatty acid esters, sucrose fatty acid esters, polyoxyethylene alkyl ethers, polyoxypropylene alkyl ethers, polyoxyethylene alkyl phenyl ethers, polyoxyethylene fatty acid esters, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbitol fatty acid esters, polyoxyethylene glycerin fatty acid esters, polyoxyethylene propylene glycol fatty acid esters, polyoxyethylene castor oil, polyoxyethylene hydrogenated castor oil, polyoxyethylene phytostanol ether, polyoxyethylene phytosterol ether, polyoxyethylene cholestanol ether, polyoxyethylene cholesteryl ether, polyoxyalkylene-modified organopolysiloxanes, organopolysiloxanes modified with both polyoxyalkylene and alkyl groups, alkanolamides, sugar ethers and sugar amides; and examples of a usable amphoteric surfactant include betaine, aminocarboxylate and imidazoline derivatives.

[0039] Furthermore, the present cosmetic material can contain powders depending on the desired purposes. Such powders are not particularly restricted as to their shape (whether it is spherical, acicular or tabular), their size (whether it is on the order of fume, fine grain or pigment), and their structure (whether it is porous or nonporous), provided that they have so far been used in conventional cosmetic materials. For instance, inorganic powders, organic powders, surfactant metal salt powders, colored pigments, pearl pigments, metallic powder pigments and natural colors can be added to the present cosmetic material, if desired.

[0040] Examples of a usable inorganic powder include titanium oxide, zirconium oxide, zinc oxide, cerium oxide, magnesium oxide, barium sulfate, calcium sulfate, magnesium sulfate, calcium carbonate, magnesium carbonate, talc, mica, kaolin, sericite, muscovite, synthetic mica, phlogopite, ruby mica, biotite, lipolite, silicic acid, silicic acid anhydride, aluminum silicate, magnesium silicate, aluminum magnesium silicate, calcium silicate, barium silicate, strontium silicate, metal salts of tungstic acid, hydroxyapatite, vermiculite, haidelite, bentonite, montmorillonite, hectorite, zeolite, ceramics powder, calcium secondary phosphate, alumina, aluminum hydroxide, boron nitride and silica.

[0041] Examples of a usable organic powder include polyamide powder, polyester powder, polyethylene powder, polypropylene powder, polystyrene powder, polyurethane powder, benzoguanamine powder, polymethylbenzoguanamine powder, polytetrafluoroethylene powder, polymethylmethacrylate powder, cellulose powder, silk powder, nylon powder such as 12-nylon powder or 6-nylon powder, silicone elastomer powder, styrene-acrylic acid copolymer powder, divinylbenzene-styrene copolymer powder, vinyl resin powder, urea resin powder, phenol resin powder, fluorescein powder, silicone resin powder, acrylic resin powder, melamine resin powder, epoxy resin powder, polycarbonate resin powder, microcrystalline fiber powder, starch powder and lauroyl lysine powder. In addition, the organic powders the main skeleton of which is $-\text{Si}(\text{O})_n-$ can be used to advantage. These silicone powders may contain $-\text{Si}-(\text{CH}_2\text{CH}_2)_m-\text{Si}-$ linkage as a part of molecular structure.

[0042] Examples of a usable surfactant metal salt powder (metal soap powder) include powders of zinc stearate, aluminum stearate, calcium stearate, magnesium stearate, zinc myristate, magnesium myristate, zinc cetylphosphate, calcium cetylphosphate and zinc sodium cetylphosphate.

[0043] Examples of a usable colored pigment include inorganic red pigments, such as iron oxide, iron hydroxide and iron titanate; inorganic brown pigments, such as γ -iron oxide; inorganic yellow pigments, such as iron oxide yellow and loess; inorganic black pigments, such as iron oxide black and carbon black; inorganic violet pigments, such as manganese violet and cobalt violet; inorganic green pigments, such as chromium hydroxide, chromium oxide, cobalt oxide and cobalt titanate; inorganic blue pigments, such as Prussian blue and ultramarine blue; lakes of tar pigments; lakes of natural dyes; and synthetic resin powder complexes of the inorganic pigments as recited above.

[0044] Examples of a usable pearl pigment include titanium oxide-coated mica, bismuth oxychloride, titanium oxide-coated bismuth oxychloride, titanium oxide-coated talc, fish scales, and titanium oxide-coated colored mica; and those of a usable metallic powder pigment include aluminum powder, copper powder and stainless powder.

[0045] The tar pigments described above include Red No. 3, Red No. 104, Red No. 106, Red No. 201, Red No. 202, Red No. 204, Red No. 205, Red No. 220, Red No. 226, Red No. 227, Red No. 228, Red No. 230, Red No. 401, Red No. 505, Yellow No. 4, Yellow No. 5, Yellow No. 202, Yellow No. 203, Yellow No. 204, Yellow No. 401, Blue No. 1, Blue No. 2, Blue No. 201, Blue No. 404, Green No. 3, Green No. 201, Green No. 204, Green No. 205, Orange No. 201, Orange No. 203, Orange No. 204, Orange No. 206 and Orange No. 207 (according to the pigment nomenclature method in JIS); and the natural pigments described above include powders of carminic acid, laccic acid, carthamin, bradilin and crocin.

[0046] Additionally, complexes of the powders as recited above or those obtained by treating the powders as recited above with general oil, silicone oil, a fluorine-containing compound or a surfactant may be used. Also, the powders as recited above may be used as a mixture of two or more thereof, if desired.

[0047] In the present cosmetic materials, the compounds having at least one alcoholic hydroxyl group per molecule can be used depending on the desired purposes of the cosmetic materials.

[0048] Examples of alcohols which can be added include lower alcohols, such as ethanol and isopropanol; sugar alcohols, such as sorbitol and maltose; and sterols, such as cholesterol, sitosterol, phytosterol and lanosterol.

5 [0049] Examples of water-soluble polymers which can be added include vegetable polymers, such as gum arabic, tragacanth, galactan, carob gum, guar gum, karaya gum, carrageenan, pectin, agar, quince seed, starch (rice, corn, potato, wheat), alge colloid, tranto gum and locust bean gum; microbial polymers, such as xanthan gum, d xtran, succinoglucan and pullulan; animal polymers, such as collagen, casein, albumin and gelatin; starch polymers, such as carboxymethyl starch and methylhydroxypropyl starch; cellulose polymers, such as methyl cellulose, ethyl cellulose, 10 methylhydroxypropyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, nitrocellulose, sodium cellulose sulfate, sodium carboxymethylcellulose, crystalline cellulose and powdery cellulose; alginic acid polymers, such as sodium alginic acid and propylene glycol ester of alginic acid; vinyl polymers, such as polyvinyl methyl ether and carboxyvinyl polymer; polyoxyethylene polymers; polyoxyethylene-polyoxypropylene copolymers; acrylic polymers, such as sodium polyacrylate, polyethylacrylate and polyacrylamide; other synthetic water-soluble polymers, 15 such as polyethylenimines and cationic polymers; and inorganic water-soluble polymers, such as bentonite, aluminum magnesium silicate, montmorillonite, beidellite, nontronite, saponite, hectorite and silicic acid anhydride.

[0050] In these water-soluble polymers, film-forming agents, such as polyvinyl alcohol and polyvinyl pyrrolidine, are also included.

20 [0051] The present cosmetic materials can further contain cross-linked organopolysiloxanes. The cross-linked organopolysiloxanes suitable for the present cosmetic materials are those which cause swelling when they contain a silicone having low viscosity of from 0.65 to 10.0 mm²/sec (25°) in a quantity larger than their self weight. Further, it is desirable that the cross-linked structure of those organopolysiloxanes be formed by the reaction between the hydrogen atoms bonded directly to silicon atoms and a cross-linking agent having at least two vinylic reactive moieties per molecule. Furthermore, it is desirable in the foregoing reaction to use the cross-linking agent containing at least one moiety selected from polyoxyalkylene, alkyl, alkenyl, aryl and fluoroalkyl moieties. The suitable proportion of such cross-linked 25 organopolysiloxanes mixed in the present cosmetic material is from 0.1 to 30.0 weight %, preferably from 1.0 to 10.0 weight %, to the total weight of the cosmetic material.

[0052] The present cosmetic material can further contain one or more of silicone resins, such as acryl-silicone graft or block copolymers and silicone compounds having network structure, if needed.

30 [0053] In particular, acrylsilicone resins are suitable for the present cosmetic material. Further, it is desirable that at least one moiety selected from the group consisting of pyrrolidone, long-chain alkyl, polyoxyalkylene and fluoroalkyl moieties be present in such an acrylsilicone resin molecule.

[0054] The other favorable silicone resins are silicone compounds having network structure. When the silicone resins, such as acryl-silicone graft or block copolymer and silicone compounds having network structure, are mixed in the 35 present cosmetic material, the appropriate proportion of silicone resins mixed is from 0.1 to 20 weight %, preferably from 1 to 10 weight %, to the total weight of the cosmetic material.

40 [0055] To the present cosmetic material, the ingredients used in general cosmetic materials, such as water, a film-forming agent, an oil-soluble gelling agent, clay minerals modified with organic compounds, resins, ultraviolet absorbents, a moisture-holding agent, antiseptics, an antimicrobial agent, perfume, salts, antioxidants, pH regulators, a chelating agent, refrigerant, an anti-inflammatory agent, skin beautifying components (a skin whitener, a cell activator, a rough dry skin improver, a blood circulation promoter, a skin astringent and an anti-seborrheic agent), vitamins, amino acids, nucleic acids, hormones and clathrate compounds, can be added so far as they have no adverse influence on the effects of the present invention.

45 [0056] Examples of an oil-soluble gelling agent which can be added include metal soaps, such as aluminum stearate, magnesium stearate and zinc myristate; amino acid derivatives, such as N-lauroyl-L-glutamic acid and α,γ-di-n-butylamine; dextrin fatty acid esters, such as dextrin palmitic acid ester, dextrin stearic acid ester and dextrin 2-ethylhexaminic acid palmitic acid ester; sucrose fatty acid esters, such as sucrose palmitic acid ester and sucrose stearic acid ester; benzylidene derivatives of sorbitol, such as monobenzylidene sorbitol and dibenzylidene sorbitol; and clay minerals modified with organic compounds, such as dimethylbenzylidodecyl ammonium montmorillonite clay and 50 dimethyldioctadecyl ammonium montmorillonite clay.

55 [0057] Examples of an ultraviolet absorbent which can be added include ultraviolet absorbents of benzoic acid type, such as p-aminobenzoic acid; those of anthranilic acid type, such as methyl anthranilate; those of salicylic acid type, such as methyl salicylate; those of succinic acid type, such as octyl p-methoxysuccinate; those of benzophenone type, such as 2,4-dihydroxybenzophenone; those of urocanic acid type, such as ethyl urocanate; and those of dibenzoylmethane type, such as 4-t-butyl-4'-methoxydibenzoylmethane.

[0058] Examples of a moisture-holding agent which can be added includ glyc rin, sorbitol, propylene glycol, dipropylene glycol, 1,3-butylene glycol, glucose, xylitol, maltitol, polyethylen glycol, hyaluronic acid, chondroitin sulfuric acid, pyrrolidone carboxylic acid, polyoxyethylene glycoside, and polyoxypropyl ne methylglycoside.

[0059] Examples of an antiseptic agent which can be added include alkyl p-hydroxybenzoates, benzoic acid, sodium benzoate, sorbic acid, potassium sorbate and phenoxyethanol; and those of an antimicrobial agent which can be added include benzoic acid, salicylic acid, carbolic acid, sorbic acid, alkyl p-hydroxybenzoates, p-chlorometacresol, hexachlorophene, benzalkonium chloride, chlorhexidine chloride, trichlorocarbanilide, photosensitizer and phenoxyethanol.

5 [0060] Examples of an antioxidant which can be added include tocopherol, butylhydroxyanisole, dibutylhydroxytoluene and phytic acid; those of a pH regulator which can be added include lactic acid, citric acid, glycolic acid, succinic acid, tartaric acid, dl-malic acid, potassium carbonate, sodium hydrogen carbonate and ammonium hydrogen carbonate; those of a chelating agent which can be added include alanine, sodium ethylenediaminetetraacetate, sodium polyphosphate, sodium metaphosphate and phosphoric acid; those of a refrigerant which can be added include L-menthol and camphor; and those of an anti-inflammatory agent which can be added include allantoin, glycyrrhizin and salts thereof, glycyrrhetic acid and stearyl glycyrrhetinate, tranexamic acid and azulene.

10 [0061] Examples of a skin-beautifying component which can be added include whitening agents, such as placenta extract, arbutin, glutathione and Yukinoshita extract; cell activators, such as royal jelly, photosensitizer, cholesterol derivatives and calf blood extract; rough dry skin improvers; blood circulation improvers, such as nonylid acid vanillyl amide, benzyl nicotinate, β -butoxyethyl nicotinate, capsaicin, zingerone, cantharis tincture, ichtammol, caffeine, tannic acid, α -borneol, tocopheryl nicotinate, inositol hexanicotinate, cyclandelate, cinnarizine, tolazoline, acetyl choline, verapamil, cepharanthin and γ -oryzanol; skin astringents, such as zinc oxide and tannic acid; and anti-seborrheic agents, such as sulfur and thianthrol.

15 [0062] Examples of vitamins which can be added include vitamin A, such as vitamin A oil, retinol, retinyl acetate and retinyl palmitate; vitamin B, including vitamin B₂ such as riboflavin, riboflavin butyrate and flavin adenine nucleotide, vitamin B₆ such as pyridoxine hydrochloride, pyridoxine dioctanoate and pyridoxine tripalmitate, vitamin B₁₂ and its derivatives, and vitamin B₁₅ and its derivatives; vitamin C, such as L-ascorbic acid, L-ascorbic acid dipalmitic ester, sodium (L-ascorbic acid)-2-sulfate and dipotassium L-ascorbic acid diphosphate; vitamin D, such as ergocalciferol and cholecalciferol; vitamin E, such as α -tocopherol, β -tocopherol, γ -tocopherol, dl- α -tocopheryl acetate, dl- α -tocopheryl nicotinate and dl- α -tocopheryl succinate; vitamin H; vitamin P; nicotinic acids, such as nicotinic acid, benzyl nicotinate and nicotinic acid amide; pantothenic acids, such as calcium pantothenate, D-pantothenyl alcohol, pantothenyl ethyl ether and acetyl pantothenyl ethyl ether; and biotin.

20 [0063] Examples of an amino acid which can be added include glycine, valine, leucine, isoleucine, serine, threonine, phenylalanine, alginine, lysine, aspartic acid, glutamic acid, cystine, cysteine, methionine, and tryptophan; those of a nucleic acid which can be added include deoxyribonucleic acid; and those of hormone which can be added include estradiol and ethenyl estradiol.

25 [0064] The term "cosmetic material" as used herein are intended to include skin care products, such as face lotion, milky lotion, cream, face cleansing cream, massage materials, toilet soap and detergent, antiperspirant and deodorant; makeup products, such as face powder, foundation, rouge, eye shadow, mascara, eyeliner and lipstick; and hairdressing products, such as shampoo, rinse and treatment.

30 [0065] Additionally, the present cosmetic material may have any of forms, including liquid, emulsion, solid, paste, gel and spray forms, if desired.

[0066] The present invention will now be illustrated in greater detail by reference to the following examples and comparative examples. However, the invention should not be construed as being limited to these examples. And the term "%" used hereinafter means "% by weight" unless noted otherwise.

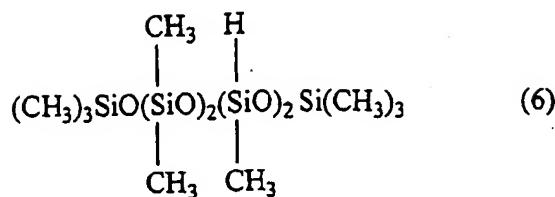
35 [0067] Additionally, the entire disclosure of all applications, patents and publications, cited above and below, and of corresponding Japanese applications No. 11-164768, filed on 11 June 1999 and No. 2000-169265, filed on 6 June 2000, is hereby incorporated by reference.

40 45 SYNTHESIS EXAMPLE 1

[0068] After 282 parts by weight of organohydrogensiloxanes represented by the following average structural formula (6) and 638 parts by weight of toluene were placed in a reaction vessel, 2 parts by weight of a 0.5 % toluene solution of chloroplatinic acid was added thereto.

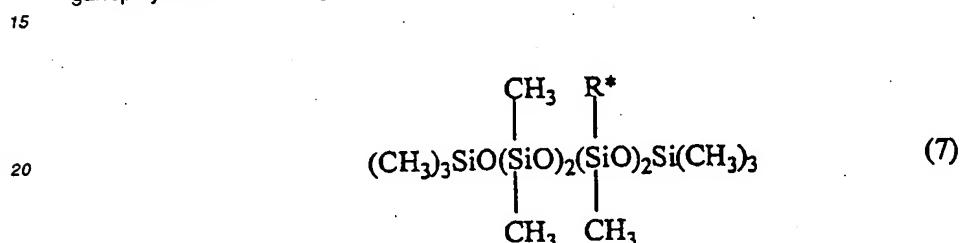
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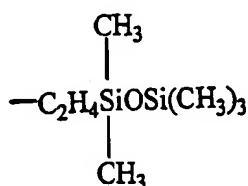


[0069] Further thereto, 356 parts by weight of pentamethyl-vinyldisiloxane was added dropwise under reflux of the solvent to undergo the reaction for 6 hours.

[0070] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, organopolysiloxanes having the following average structural formula (7) were obtained.



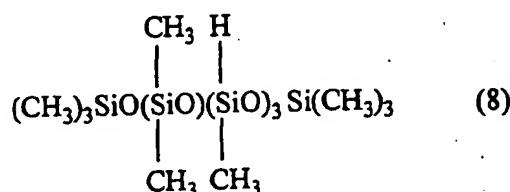
[0071] Therein, -R* represents



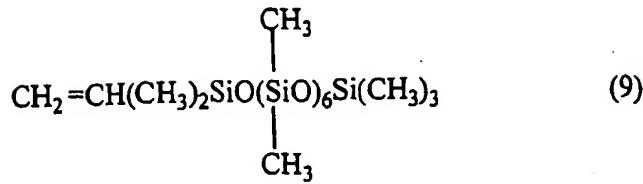
[0072] The product obtained was colorless transparent liquid, and it had a viscosity of 7 mm²/s (at 25°C) and a specific gravity of 0.885 (at 25°C).

40 SYNTHESIS EXAMPLE 2

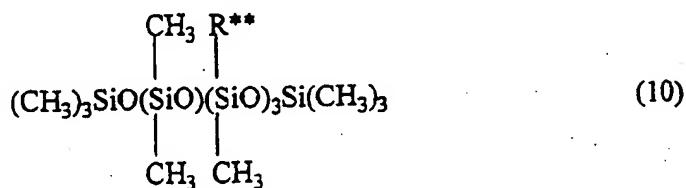
[0073] After 208 parts by weight of organohydrogensiloxanes represented by the following average structural formula (8) and 638 parts by weight of toluene were placed in a reaction vessel, 2 parts by weight of a 0.5 % toluene solution of chloroplatinic acid was added thereto.



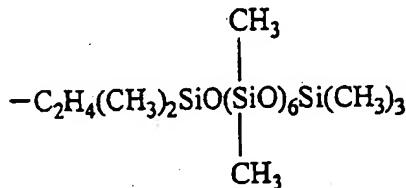
[0074] Further thereto, 1,100 parts by weight of organopolysiloxanes having the following structural formula (9) were added dropwise under reflux of the solvent to undergo the reaction for 6 hours.



[0075] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, organopolysiloxanes having the following average structural formula (10) were obtained.



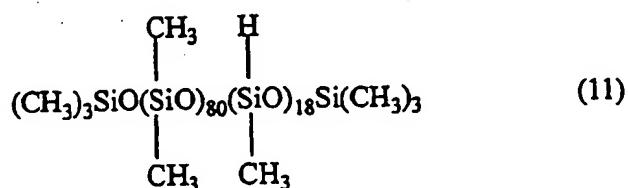
[0076] Therein, -R^{**} represents



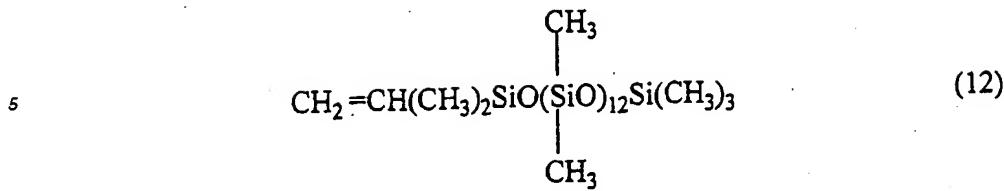
[0077] The product obtained was colorless transparent liquid, and it had a viscosity of 32 mm²/s (at 25°C) and a specific gravity of 0.947 (at 25°C).

SYNTHESIS EXAMPLE 3

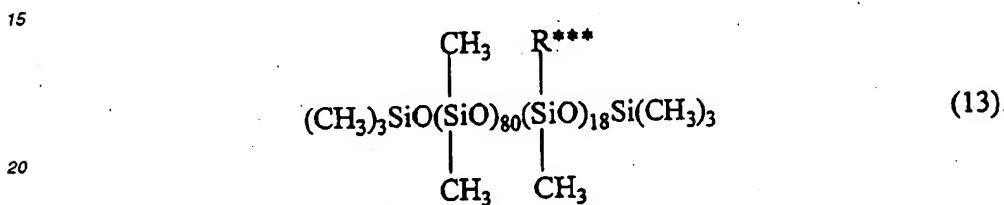
40 [0078] After 293 parts by weight of organohydrogensiloxanes represented by the following average structural formula (11) and 1,300 parts by weight of toluene were placed in a reaction vessel, 2 parts by weight of a 0.5 % toluene solution of chloroplatinic acid was added thereto.



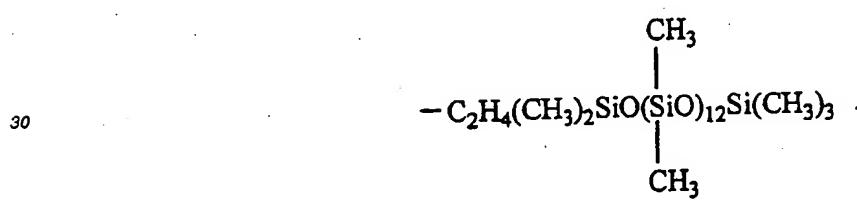
[0079] Further thereto, 1,000 parts by weight of organopolysiloxanes having the following structural formula (12) were added dropwise under reflux of the solvent to undergo the reaction for 6 hours.



10 [0080] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, organopolysiloxanes having the following average structural formula (13) were obtained.



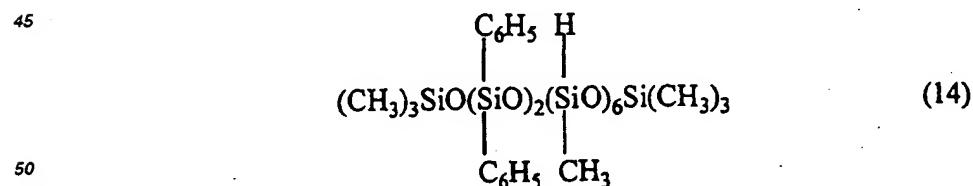
25 [0081] Therein, R*** represents



35 [0082] The product obtained was colorless transparent liquid, and it had a viscosity of 300 mm²/s (at 25°C) and a specific gravity of 0.963 (at 25°C).

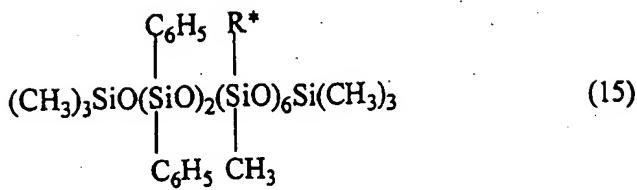
SYNTHESIS EXAMPLE 4

40 [0083] After 409 parts by weight of organohydrogensiloxanes represented by the following average structural formula (14) and 490 parts by weight of toluene were placed in a reaction vessel, 2 parts by weight of a 0.5 % toluene solution of chloroplatinic acid was added thereto.



[0084] Further thereto, 530 parts by weight of pentamethyl-vinyldisiloxane was added dropwise under reflux of the solvent to undergo the reaction for 6 hours.

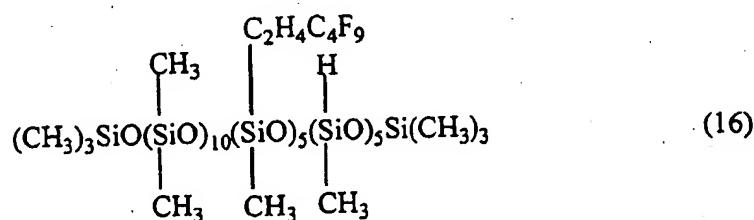
55 [0085] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, organopolysiloxanes having the following average structural formula (15) were obtained.



[0086] Therein, -R* has the same meaning as in Synthesis Example 1.
[0087] The product obtained was colorless transparent liquid, and it had a viscosity of 230 mm²/s (at 25°C) and a specific gravity of 0.977 (at 25°C).

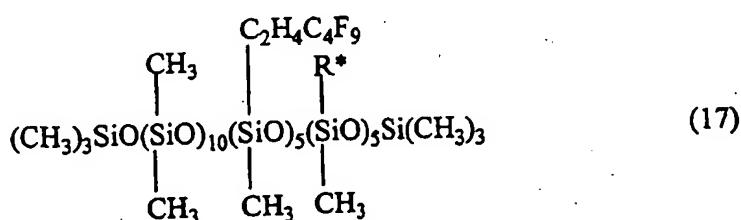
SYNTHESIS EXAMPLE 5

[0088] After 546 parts by weight of organohydrogensiloxanes represented by the following average structural formula (16) and 360 parts by weight of toluene were placed in a reaction vessel, 0.2 parts by weight of a 2 % toluene solution of chloroplatinic acid was added thereto.



[0089] Further thereto, 174 parts by weight of pentamethyl-vinyldisiloxane was added dropwise under reflux of the solvent to undergo the reaction.

[0090] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, or-
ganopolysiloxanes having the following average structural formula (17) were obtained.

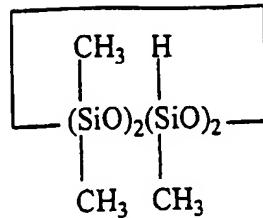


[0091] Therein, R¹ has the same meaning as in Synthesis Example 1.
[0092] The product obtained was colorless transparent liquid, and it had a viscosity of 113 mm²/s (at 25°C) and a specific gravity of 1.126 (at 25°C).

SYNTHESIS EXAMPLE 6

[0093] After 268 parts by weight of cyclosiloxanes represented by the following average structural formula (18) and 300 parts by weight of toluene were placed in a reaction vessel, 0.2 parts by weight of a 2% toluene solution of chloroplatinic acid was added thereto.

5



(18)

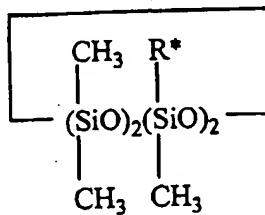
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[0094] Further thereto, 348 parts by weight of pentamethyl-vinylsiloxane was added dropwise under reflux of the solvent to undergo the reaction.

[0095] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, organopolysiloxanes having the following average structural formula (19) were obtained.

15

20



(19)

25

[0096] Therein, R* has the same meaning as in Synthesis Example 1.

[0097] The product obtained was colorless transparent liquid, and it had a viscosity of 12 mm²/s (at 25°C) and a specific gravity of 0.930 (at 25°C).

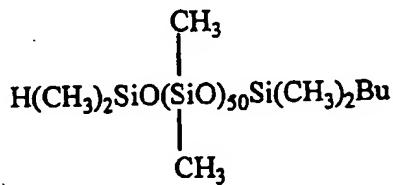
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SYNTHESIS EXAMPLE 7

[0098] In a reaction vessel were placed 200 parts by weight of methylvinylpolysiloxanes having a vinyl value of 0.135 mole/100g, 920 parts by weight of organopolysiloxanes having the following average structural formula (20) and 1,000 parts by weight of toluene. Further thereto was added 2 parts by weight of 0.5 % of toluene solution of chloroplatinic acid. Therein, the reaction was carried out for 6 hours under reflux of the solvent. Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, silicone-grafted organopolysiloxanes were obtained. This product was colorless transparent liquid, and it had a viscosity of 1,800 mm²/s (at 25°C) and a specific gravity of 0.968 (at 25°C).

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(20)

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SYNTHESIS EXAMPLE 8

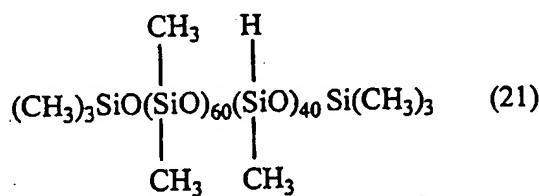
[0099] In a reaction vessel, 1,000 parts by weight of the silicone-grafted organopolysiloxanes obtained in Synthesis Example 7 and 200 parts by weight of organopolysiloxane gum were placed, and mixed with stirring. Thus, silicone gum solution having a viscosity of 40,000 mPa·s (25°C) was obtained.

SYNTHESIS EXAMPLE 9

[0100] In a reaction vessel, 700 parts by weight of a toluene solution of silicone resin having a weight average molecular weight of 4,700 (the resin concentration was 72 %) and 520 parts by weight of the silicone-grafted organopolysiloxanes obtained in Synthesis Example 6 were placed. The contents in the vessel were heated up to 120°C under reduced pressure, thereby distilling off the toluene therefrom. Further, the temperature inside the vessel was raised to 130°C to distill off 30 parts by weight of the silicone-grafted organopolysiloxane, and to thoroughly distill off the toluene. After filtration and subsequent adjustment of volatile components, 1,000 parts by weight of a 50 % siloxane solution of silicone resins was obtained.

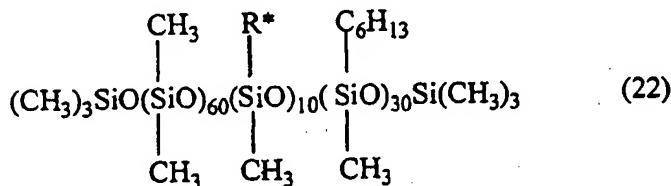
SYNTHESIS EXAMPLE 10

[0101] After 715 parts by weight of organohydrogensiloxanes represented by the following average structural formula (21) and 700 parts by weight of toluene were placed in a reaction vessel, 2 parts by weight of a 0.5 % toluene solution of chloroplatinic acid was added thereto.



[0102] Further thereto, 174 parts by weight of pentamethyl-vinyldisiloxane was added dropwise under reflux of the solvent to undergo the reaction. Furthermore, 252 parts by weight of 1-hexene was added dropwise thereto. And the reaction was continued for 6 hours.

[0103] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, organopolysiloxanes having the following average structural formula (22) were obtained.

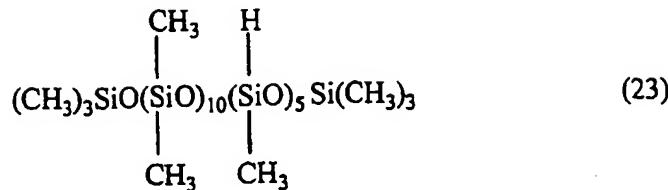


[0104] Therein, -R* has the same meaning as in Synthesis Example 1.

[0105] The product obtained was colorless transparent liquid, and it had a viscosity of 500 mm²/s (at 25°C) and a specific gravity of 0.945 (at 25°C).

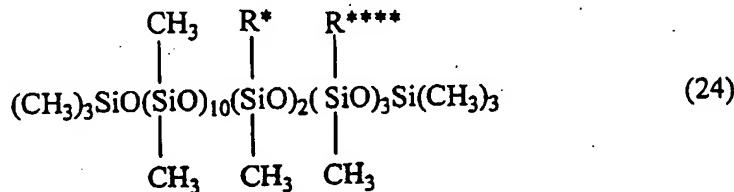
SYNTHESIS EXAMPLE 11

[0106] After 480 parts by weight of organohydrogensiloxanes represented by the following average structural formula (23) and 1,000 parts by weight of toluene were placed in a reaction vessel, 0.2 parts by weight of a 2 % toluene solution of chloroplatinic acid was added thereto.



[0107] Further thereto, 600 parts by weight of the organopolysiloxanes represented by the foregoing average structural formula (9) was added dropwise under reflux of the solvent to undergo the reaction for 2 hours. Furthermore, 780 parts by weight of a 50 % toluene solution of allylstearate was added dropwise thereto. And the reaction was continued for 3 hours.

[0108] Then, the reaction mixture was heated under reduced pressure to distill off the solvent therefrom. Thus, organopolysiloxanes having the following average structural formula (24) were obtained.



[0109] Therein, $-R^*$ has the same meaning as in Synthesis Example 1, and $-R^{****}$ stands for $-C_3H_6OC(=O)C_{17}H_{35}$.
 [0110] The product obtained was colorless transparent liquid, and it had a viscosity of 70 mm²/s (at 25°C) and a

[0110] The product obtained was colorless transparent liquid, and it had a viscosity of 70 mNP/s (at 25°C) and a specific gravity of 0.947 (at 25°C).

EXAMPLES 1 TO 2 AND COMPARATIVE EXAMPLES 1 TO 5

[0111] The ingredients Nos. 1 to 11 set forth in Table 1 were each heated and mixed together to be made into a homogeneous solution. Therein, the ingredients Nos. 12 to 14 set forth in Table 1 were further dispersed homogeneously. Then, the ingredients Nos. 15 to 18 were added thereto, and the composition obtained was packed in cases. Thus, lipstick samples were produced.

40

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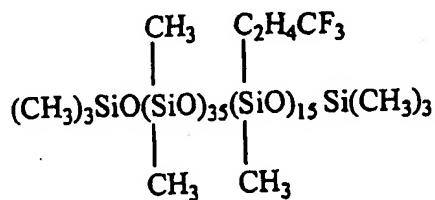
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Table 1

No.	Ingredient (weight %)	Example		Comparative Example				
		1	2	1	2	3	4	5
1	Polyethylene-poly-propylene copolymer	5	5	5	5	5	5	5
2	Candelilla wax	5	5	5	5	5	5	5
3	Ceresin wax	5	5	5	5	5	5	5
4	Micocrystalline wax	-	-	-	5	10	-	-
5	Vaseline	10	10	10	10	10	10	10
6	Cetyl 2-ethylhexanoate	16	11	16	11	16	11	16
7	Glyceryl trioctanoate	35	35	35	35	35	35	35
8	Glyceryl trisostearate	5	5	5	5	5	5	5
9	Dimethylpoly-siloxane (6 mm ² /s)	-	-	5	10	-	-	-
10	Fluorine-modified silicone ^(*)	-	-	-	-	-	-	5
11	Grafted silicone of Synthesis Example 5	5	10	-	-	-	-	-
12	Pigment	5	5	5	5	5	5	5
13	Silicone-treated titanium oxide	4	4	4	4	4	4	4
14	Silicone-treated titanium mica	5	5	5	5	5	5	5
15	Beautifying component	Respectively proper amounts						
16	Ultraviolet absorbent							
17	Antiseptic							
18	Perfume							

(*) Fluorine-modified silicone:



[0112] The ease-of-use, luster, makeup durability and smear resistance of the lipstick samples obtained were evaluated by 50 female panelists in accordance with the criteria shown in Table 2.

Table 2

Marks	Ease-of-use Makeup durability	Spread	Smear resistance
5	good	light	good
4	fairly good	fairly light	Fairly good
3	average	average	average
2	rather bad	rather heavy	rather poor
1	bad	heavy	poor

[0113] Judging from the average of marks given by the panelists, the quality of lipstick prepared in each Example was assessed in accordance with the standards described below:

<Assessment Standards for Average Mark>	
Average mark obtained	Symbol (Quality)
4.5 or above	◎(good)
from 3.5 to lower than 4.5	○ (fairly good)
from 2.5 to lower than 3.5	△ (average)
from 1.5 to lower than 2.5	X (rather bad)
lower than 1.5	XX (bad)

[0114] The evaluation results according to the aforementioned assessment standards are shown in Table 3.

Table 3

Item	Example		Comparative Example				
	1	2	1	2	3	4	5
Ease-of-use	◎	◎	○	○	×	XX	△
Spread	◎	◎	○	○	△	XX	○
Smear resistance	○	○	×	XX	△	○	△
Makeup durability	○	○	×	XX	△	○	○

[0115] As can be seen from Table 3, it has been demonstrated that the lipsticks prepared in Examples 1 and 2 spread well and had satisfactory usability, high smear resistance and good makeup durability, compared with those prepared in Comparative Examples 1 to 5.

EXAMPLE 3

[0116] Milky lotion containing the following ingredients was prepared:

Ingredients		Amount mixed (%)
1.	N-acylglutamic acid	0.1
2.	1,3-Butylene glycol	0.4
3.	Glycerol mono fatty acid ester	0.5
4.	Cetanol	0.5
5.	Spermaceti	1.0
6.	Glyceryl trioctanoate	8.0
7.	Grafted silicone of Synthesis Example 3	6.0
8.	Sodium hydroxide	0.025
9.	1,3-Butylene glycol	15.0
10.	Purified water	the rest

[Preparation Process]

[0117] The milky lotion was prepared following the steps A to C described below:

5 (A) The ingredients 1 and 2 were mixed together under heating to prepare a solution.
 (B) The solution was admixed with the ingredients 3 to 7, and this mixture was kept at 75°C.
 (C) The ingredients 8 to 10 were mixed together and dissolved homogeneously by heating at 75°C. This solution
 was added to the foregoing mixture kept at 75°C, and emulsified, and then cooled to prepare milky lotion.

10 [0118] It has been confirmed that the thus prepared milky lotion not only formed a water-repellent film but also created
 a feeling of being moisturized when applied to the skin, and besides, it provided a pleasant feel and ease of use to the
 users.

EXAMPLE 4

15 [0119] The following ingredients were mixed together, and made into compressed face powder in accordance with
 the process described below:

Ingredients	Amount mixed (%)
1. Silicone-treated rutile-type titanium oxide	10.0
2. Silicone-treated anatase-type titanium oxide	2.0
3. Silicone-treated sericite (oil treatment with vaseline)	35.0
4. Lecithin-treated talc	35.1
5. Lecithin-treated spherical nylon powder	5.0
6. Iron oxide red	0.4
7. Iron oxide yellow	2.0
8. Amber	0.4
9. Iron oxide black	0.1
10. Grafted silicone of Synthesis Example 4	7.0
11. Glyceryl trioctanoate	1.5
12. Dipentaerythritol fatty acid ester	1.5

[Preparation Process]

[0120] The compressed face powder was prepared following the steps A and B described below:

40 (A) The ingredients 1 to 9 were mixed together, and then ground to homogeneous powder A.
 (B) The powder A was admixed with the ingredients 10 to 12, ground to homogeneous powder, and then com-
 pressed tightly into a metal pan.

[0121] The face powder thus compressed spread lightly and smoothly, stayed well due to its good adhesion and was
 highly resistant to sweat. Thus, the present face powder can produce makeup effect of long duration, and provide a
 pleasant feel and excellent usability to the users.

EXAMPLE 5

[0122] An overcoat composition constituted of the following ingredients was prepared:

Ingredients	Amount mixed (%)
1. Polyethylene/polypropylene copolymer	10
2. Ceresin wax	10
3. Glyceryl trioctanoate	30
4. Grafted silicone of Synthesis Example 2	30
5. Dimethylcyclopentasiloxane	20

[Preparation Process]

[0123] The overcoat composition was prepared following the steps A and B described below:

5 (A) The ingredients 1 to 5 were mixed together to prepare a homogeneous solution.
 (B) The solution obtained was charged into vessels.

[0124] It was confirmed that the thus prepared overcoat composition spread well, had excellent usability, extended the duration of makeup effect, and provided lasting moisture and luster.

10 EXAMPLE 6

[0125] A makeup remover constituted of the following ingredients was prepared:

Ingredients		Amount mixed (%)
1.	Grafted silicone of Synthesis Example 1	20.0
2.	Polyoxyethylene(20) sorbitan monostearate	10.0
3.	Sorbitol	10.0
4.	Carrageenan	0.5
5.	Antiseptic	proper
6.	Perfume	proper
7.	Purified water	rest

25 [Preparation Process]

[0126] The makeup remover was prepared following the steps A and B described below:

30 (A) The ingredients 1 to 5 and 7 were mixed together to prepare a homogeneous solution.
 (B) The ingredient 6 was added to the solution.

[0127] The thus prepared makeup remover was used for removing durable face powder. As a result, it was found that the face powder and the sebum stains absorbed this remover well and they came out easily. Further, the remover spread well and had no sticky feel when applied to the face, and left a refreshed feel to the face after it was wiped off. In other words, this remover had excellent usability and provided a pleasant feel to the users. In addition, it has proved that the remover caused no change by fluctuation in temperature and passage of time, namely it had high stability.

35 EXAMPLE 7

40 [0128] A hair makeup remover constituted of the following ingredients was prepared:

Ingredients		Amount mixed (%)
1.	Grafted silicone of Synthesis Example 5	10.0
2.	Diethylene glycol monoethyl ether	5.0
3.	Glycerin	30.0
4.	Carrageenan	0.5
5.	Antiseptic	proper
6.	Perfume	proper
7.	Purified water	rest

45 [Preparation Process]

50 [0129] The hair-makeup remover was prepared following the steps A and B described below:

(A) The ingredients 1 to 5 and 7 were mixed together to prepare a homogeneous solution.
 (B) The ingredient 6 was added to the solution.

[0130] The hair was washed with the thus prepared hair-makeup remover. As a result, it was found that the hair makeup and the sebum stains absorbed this remover well and they came out easily. Further, the remover spread well when applied to the hair, and had no sticky feel but left a refreshed feel to the users after it was washed out. In other words, this remover had excellent usability and provided a pleasant feel to the users. In addition, it was confirmed that the remover caused no change by fluctuation in temperature and passage of time, namely it had high stability.

5

EXAMPLE 8

[0131] Hair cream constituted of the following ingredients was prepared:

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Ingredients		Amount mixed (%)
1.	Silicone gum solution of Synthesis Example 8	18
2.	Silicone resin solution of Synthesis Example 9	6
3.	Glyceryl tri-2-ethylhexanoate	8
4.	Vaseline	5
5.	Stearyl alcohol Stearyl alcohol	2
6.	Sorbitan monooleate	2
7.	Polyoxyethylene (50) hydrogenated castor oil	2
8.	Glycerol	5
9.	Perfume	proper
10.	Purified water	the rest

15

20

25

[Preparation Process]

[0132] The hair cream was prepared following the steps A and B described below:

30

- (A) The ingredients 1 to 7 were mixed together, and made into a solution by heating at 70°C.
- (B) The ingredients 8 to 10 were mixed together with stirring, and thereto the solution obtained in the step A was added, followed by emulsification.

[0133] The thus prepared hair cream was found to give fine luster and smoothness to the hair and have excellent setting effect on the hair.

35

EXAMPLE 9

[0134] Lipstick containing the following ingredients was prepared:

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Ingredients		Amount mixed (%)
1.	Polyethylene wax	15
2.	Candelilla wax	3
3.	Microcrystalline wax	2
4.	Pentaerythritol stearate	5
5.	Cetyl isoctanoate	31
6.	Propylene glycol didecanoate	17
7.	Grafted silicone of Synthesis Example 10	27
8.	Pigment	0.5

[Preparation Process]

[0135] The lipstick was prepared following the steps A and B described below:

55

- (A) The ingredients 1 to 7 were mixed together at 90°C.
- (B) Thereto, the ingredient 8 was added, and dispersed homogeneously. Then, the composition obtained was poured into cases, and cooled.

[0136] It has been shown that the thus prepared lipstick spread well and had satisfactory usability, high smear resistance and good makeup durability.

EXAMPLE 10

5

[0137] Skin cream constituted of the following ingredients was prepared:

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Ingredients		Amount mixed (%)
1.	Grafted silicone of Synthesis Example 11	3.0
2.	Grafted silicone of Synthesis Example 6	5.0
3.	Cetanol	6.0
4.	Liquid paraffin	2.0
5.	Palmitic acid	1.0
6.	Squalane	1.0
7.	Dimethylsilicone (viscosity: 50 mm ² /s)	1.0
8.	Sorbitan monostearate	2.0
9.	Sodium laurylpolyoxyethylene (4EO) sulfate	1.0
10.	Glycerin	10.0
11.	Purified water	the rest

[Preparation Process]

25

[0138] The hair cream was prepared following the steps A to C described below:

30

- (A) The ingredients 1 to 9 were mixed together, and made into a solution.
- (B) The ingredients 10 and 11 were mixed together, and made into a solution.
- (C) The solution obtained in the step B was added gradually to the solution obtained in the step A, followed by emulsification.

[0139] It has been shown that the thus prepared emulsion had excellent storage stability, a moist feel and high usability, and gave a feeling of comfort to the users.

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EXAMPLE 11

[0140] A transparent gel antiperspirant having the following composition was prepared:

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Ingredients		Amount mixed (%)
1.	KSG-21	8.0
2.	Grafted silicone of Synthesis Example 1	12.0
3.	Dipropylene glycol	16.0
4.	Aluminum zirconium tetrachlorohydrex (GLY)	20.0
5.	Water	44.0
KSG-21: Cross-linked polyether-modified methylpolysiloxane/dimethylpolysiloxane copolymer		

[Preparation Process]

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[0141] The transparent antiperspirant gel was prepared following the steps A to D described below:

55

- (A) The ingredients 1 and 2 were mixed homogeneously.
- (B) The ingredient 3 was mixed homogeneously with the mixture obtained in the step A.
- (C) The ingredients 4 and 5 were mixed homogeneously.
- (D) The mixture obtained in the step C was gradually added to the mixture obtained in the step B with stirring.

[0142] The thus obtained transparent antiperspirant gel spread smoothly, had neither tacky nor oily feel but a moist

and fresh feel, gave a refreshing feeling to the users, and caused no change in quality by temperature and aging. Further, the duration of its effect was long. In other words, the transparent antiperspirant gel according to the invention had excellent usability and stability.

5 EXAMPLE 12

[0143] Foundation cream having the following composition was prepared:

Ingredients		Amount mixed (%)
1.	KSG-21	7.0
2.	Glyceryl tri(2-ethylhexanoate)	3.0
3.	Grafted silicone of Synthesis Example 1	8.0
4.	Sodium chloride	0.5
5.	1,3-Butylene glycol	7.0
6.	KSP-100	1.5
7.	Pigment (treated so as to have hydrophobicity)	10.0
8.	KSP-545	5.0
9.	Purified water	58.0
KSP-21: Cross-linked polyether-modified methylpolysiloxane/dimethylpolysiloxane copolymer		
KSP-100: Cross-linked silicone-netted silicone block copolymer		
KSP-545: Alkyl acrylate copolymer methylpolysiloxane ester/decamethylcyclopentasiloxane mixture		

25 [Preparation Process]

[0144] The foundation cream was prepared following the steps A to D described below:

- (A) The ingredients 1 to 3 were mixed homogeneously.
- (B) The ingredient 4 was dissolved in the ingredient 9, and then added to the mixture obtained in the step A, followed by emulsification.
- (C) The ingredient 6 was dispersed in the ingredient 5, and then admixed with the emulsion obtained in the step B.
- (D) The ingredient 7 was dispersed in the ingredient 8, and then admixed with the mixture obtained in the step C.

35 [0145] The thus prepared foundation cream had a light touch, formed a film having no tacky feel but a smooth feel, and ensured a long duration of makeup effect.

EXAMPLE 13

40 [0146] A sunscreen water-in-oil emulsion having the following composition was prepared:

Ingredients		Amount mixed (%)
1.	Titanium dioxide (treated with stearic acid)	20.0
2.	KP-571	5.0
3.	Grafted silicone of Synthesis Example 6	28.0
4.	Glyceryl tri(2-ethylhexanoate)	5.0
5.	Grafted silicone of Synthesis Example 1	4.0
6.	2-Ethylhexyl paramethoxycinnamate	5.0
7.	KP-6017	1.5
8.	KP-6026	1.0
9.	1,3-Butylene glycol	4.0
10.	Purified water	26.5
KP-571: Vinylpyrrolidone/methacryl-modified methylpolysiloxane copolymer		
KP-6017: Polyoxyethylene/methylpolysiloxane copolymer		
KP-6026: Polyoxyethylene methylsiloxane/polyoxypropyl neoleylmethylsiloxane/dimethylsiloxane terpolymer		

[Preparation Process]

[0147] The preparation of the above sunscreen water-in-oil emulsion was carried out following the steps A to C described below:

5

- (A) A part of the ingredient 3 and the ingredients 4 to 8 were mixed homogeneously.
- (B) The ingredient 9 was dissolved in the ingredient 10, and then added to the mixture obtained in the step A, followed by emulsification.
- (C) The ingredients 1 and 2 and the remainder of the ingredient 3 were mixed and dispersed, and further admixed with the emulsion obtained in the step B.

10

[0148] Although a large amount of powder was mixed in the sunscreen water-in-oil emulsion thus prepared, the emulsion had low viscosity, and didn't render the emulsion-applied skin white. Further, the emulsion had excellent adhesiveness although the dispersant used therein was liquid oil, and formed a soft and natural sunscreen coating.

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EXAMPLE 14

[0149] A sunscreen water-in-oil emulsion having the following composition was prepared:

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	Ingredients	Amount mixed (%)
1.	Grafted silicone of Synthesis Example 6	15.0
2.	Methylphenylpolysiloxane	5.0
3.	Squalane	5.0
4.	Pentaerythritol tetra(2-ethylhexanoate)	5.0
5.	Polyether-modified silicone ¹⁾	3.0
6.	Organopolysiloxane elastomer spherical powder ²⁾	2.0
7.	Hydrophobic silica ³⁾	0.5
8.	Magnesium ascorbate phosphate	1.0
9.	Sodium chloride	1.0
10.	Polyethylene glycol 11000	1.0
11.	Propylene glycol	8.0
12.	Antiseptic	proper
13.	Perfume	proper
14.	Purified water	rest

1: KF-6017 (produced by Shin-etsu Chemical Co., Ltd.)

2: KMP594 (produced by Shin-etsu Chemical Co., Ltd.)

3: Aerosil R972 (produced by Nippon Aerosil Co., Ltd.)

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[Preparation Process]

[0150] The preparation of the above emulsion was carried out following the steps A to C described below:

45

- (A) The ingredients 1 to 5 were mixed homogeneously, and thereto the ingredients 6 and 7 was added, and further made into a homogeneous dispersion.
- (B) The ingredients 8 to 10 were added to the ingredient 14, and thereto the homogeneous mixture of the ingredients 11 and 12 was added.
- (C) The mixture obtained in the step B was added gradually to the dispersion obtained in the step A to make an emulsion. After the emulsion was cooled, the ingredient 13 was added thereto.

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[0151] The thus prepared emulsion spread smoothly, had no tacky feel but a dry feel, and caused no change in quality by temperature and aging. In other words, it was confirmed that the present emulsion had excellent usability and stability.

55

EXAMPLE 15

[0152] Eye wrinkle cream having the following composition was prepared:

	Ingredients	Amount mixed (%)
1.	Grafted silicone of Synthesis Example 6	20.0
2.	Timethylsiloxysilicate	5.0
3.	Polyether-modified siloxane ¹⁾	2.0
4.	Polyether- and oleyl-modified silicone ²⁾	5.0
5.	Sodium chondroitin sulfate	2.0
6.	Sodium lactate	1.0
7.	Glycerin	50.0
8.	Antiseptic	proper
9.	Antioxidant	proper
10.	Perfume	proper
11.	Purified water	rest

1) KF-6017 (produced by Shin-etsu Chemical Co., Ltd.)

2) KF-6026 (produced by Shin-etsu Chemical Co., Ltd.)

[Preparation Process]

[0153] The preparation of the above eye wrinkle cream was carried out following the steps A to C described below:

- (A) The ingredients 1 to 4 and the ingredient 9 were mixed under heating.
- (B) The ingredients 5 to 8 and the ingredient 11 were mixed under heating, and thereby a solution was made.
- (C) The solution obtained in the step B was added gradually to the mixture obtained in the step A with stirring, thereby preparing an emulsion. After the emulsion was cooled, the ingredient 10 was added thereto.

[0154] The thus prepared eye wrinkle cream spread lightly, had neither tacky nor oily feel but a moist and fresh feel, gave a refreshing feeling to the users, and caused no change in quality by temperature and aging. In other words, the eye wrinkle cream according to the invention had excellent usability and stability.

ADVANTAGES OF THE INVENTION

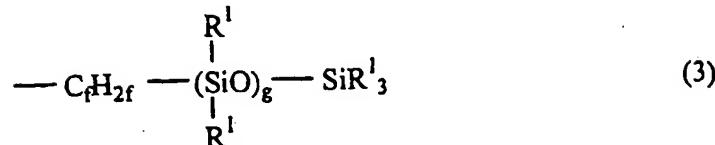
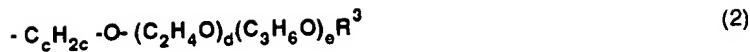
[0155] When the cosmetics in which the present silicone compounds represented by formula (1) are mixed are put on the skin, they spread smoothly, have no oily feel, and render the skin moist, fresh and youthful. Further, they provide a refreshed feel and durable makeup effect to the users, and besides, cause no change by fluctuation of temperature and passage of time, namely have very high stability. When the present silicone compounds are mixed in skin cleansing compositions, on the other hand, the resulting compositions acquire a characteristic that they absorb cosmetics and sebum stains very well and remove them efficiently in addition to having the foregoing characteristics, such as use comfort, excellent usability and high stability to aging.

Claims

1. A cosmetic material containing a silicone compound represented by the following formula (1):



wherein R¹ groups, which are the same or different, each represent a hydrogen atom or an organic group selected from the class consisting of alkyl groups containing 1 to 30 carbon atoms, aryl groups, aralkyl groups, fluorinated alkyl groups and organic groups represented by the following formula (2); R² groups each represent a silicone group represented by the following formula (3); a is a number of from 1.0 to 2.5; b is a number of from 0.001 to 1.5;



wherein R^3 is a hydrocarbon group containing 4 to 30 carbon atoms, or an organic group represented by $\text{R}^4\text{-(CO)-}$; R^4 is a hydrocarbon group containing 1 to 30 carbon atoms; c is an integer of from 0 to 15, d is an integer of from 0 to 50, and e is an integer of from 0 to 50; and f is an integer of from 1 to 5, and g is an integer of from 0 to 500.

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2. A cosmetic material according to claim 1; further containing oils as a constituent.
3. A cosmetic material according to claim 2, wherein at least one of the oils is in a liquid state at room temperature.
4. A cosmetic material according to claim 2; wherein all or at least one of the oils is a silicone oil containing volatile silicones, a silicone oil having constitutional repeating units represented by $[\text{O-Si}]_n$ in its molecular skeleton, or a mixture thereof.
5. A cosmetic material according to claim 2, 3 or 4; wherein all or at least one of the oils is an oil having fluorine-containing or amino groups.
6. A cosmetic material according to any of claims 1 to 5; further containing at least one ingredient selected from the group consisting of surfactants, powders and coloring materials.
7. A cosmetic material according to claim 6, wherein the surfactants are modified silicones having polyoxyalkylene chains.
8. A cosmetic material according to claim 6 or 7, wherein the surfactants are compounds having their HLB values in the range of 2 to 8.
9. A cosmetic material according to any of claims 6 to 8, wherein all or a part of the powder, the coloring material or the mixture thereof is an organic powder constituted of a silicone resin powder, a powder having a silicone elastomer as its skeleton, an organic powder containing constitutional repeating units represented by $[\text{O-Si}]_n$ or a mixture of two or more thereof.
10. A cosmetic material according to claim 1; further containing water as a constituent.
11. A cosmetic material according to any of claims 1 to 10; further containing as a constituent a compound having an alcoholic hydroxyl group in its molecular structure.
12. A cosmetic material according to claim 11, wherein the compound having an alcoholic hydroxyl group in its molecular structure is a monohydric water-soluble alcohol, a polyhydric water-soluble alcohol or a mixture thereof.
13. A cosmetic material according to claim 11, wherein the compound having an alcoholic hydroxyl group in its molecular structure is a water-soluble polymer.
14. A cosmetic material according to any of claims 1 to 13; further containing cross-linked organopolysiloxanes as a constituent.
15. A cosmetic material according to claim 14, wherein the cross-linked organopolysiloxanes are cross-linked organopolysiloxanes which cause swelling when they contain a silicone having low viscosity of from 0.65 to 10.0 mm²/s.

sec (25°) in a quantity larger than their self weight.

- 5 16. A cosmetic material according to claim 14 or 15, wherein the cross-linked organopolysiloxanes are organopolysiloxanes having a cross-linked structure formed by the reaction between the hydrogen atoms bonded directly to silicon atoms and a cross-linking agent having at least two vinylic reactive moieties per molecule.
- 10 17. A cosmetic material according to any of claims 14 to 16, wherein the cross-linked organopolysiloxanes are organopolysiloxanes having in their cross-links at least one kind of moiety selected from the family consisting of polyoxyalkylene, alkyl, alkenyl, aryl and fluoroalkyl moieties.
- 15 18. A cosmetic material according to any of claims 1 to 17; further containing silicone resin as a constituent.
- 20 19. A cosmetic material according to claim 18, wherein the silicone resin is an acrylsilicone resin.
- 25 20. A cosmetic material according to claim 18 or 19, wherein the silicone resin is an acrylsilicone resin containing at least one moiety selected from the group consisting of pyrrolidone, long-chain alkyl, polyoxyalkylene and fluoroalkyl moieties.
- 30 21. A cosmetic material according to claim 18, wherein the silicone resin is a silicone compound having network structure.
- 35 22. A cosmetic material according to claim 21, wherein the silicone compound having network structure is a netted silicone compound containing at least one moiety selected from the group consisting of pyrrolidone, long-chain alkyl, polyoxyalkylene, fluoroalkyl and amino moieties.
- 40 23. A skincare cosmetic material comprising the cosmetic material according to any of claims 1 to 22.
- 45 24. A hair-care cosmetic material comprising the cosmetic material according to any of claims 1 to 22.
- 50 25. An antiperspirant cosmetic material comprising the cosmetic material according to any of claims 1 to 22.
- 55 26. A makeup cosmetic material comprising the cosmetic material according to any of claims 1 to 22.
- 60 27. An UV protective cosmetic material comprising the cosmetic material according to any of claims 1 to 22.
- 65 28. A cosmetic material according to any of claims 1 to 27, which is prepared in a state selected from among the states of liquid, emulsion, cream, solid, paste, gel, powder, multilayer, mousse and spray.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 30 4947

DOCUMENTS CONSIDERED TO BE RELEVANT			Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.)		
Category	Citation of document with indication, where appropriate, of relevant passages					
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 040 (C-1155), 21 January 1994 (1994-01-21) & JP 05 262987 A (SHIN ETSU CHEM CO LTD), 12 October 1993 (1993-10-12) * abstract *	-----		A61K7/48 A61K7/06 A61K7/32 A61K7/02 A61K7/40 C08G77/50		
A	EP 0 545 002 A (KOSE CORP ; SHINETSU CHEMICAL CO (JP)) 9 June 1993 (1993-06-09)	-----				
D,A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 068 (C-0807), 18 February 1991 (1991-02-18) & JP 02 295912 A (SHISEIDO CO LTD), 6 December 1990 (1990-12-06) * abstract *	-----				
D,A	US 5 557 000 A (MINEMURA MASAHIKO) 17 September 1996 (1996-09-17) & JP 07 197055 A 1 August 1995 (1995-08-01)	-----		TECHNICAL FIELDS SEARCHED (Int.Cl.)		
				A61K C08G		
The present search report has been drawn up for all claims						
Place of search		Date of completion of the search	Examiner			
THE HAGUE		18 October 2000	Stienon, P			
CATEGORY OF CITED DOCUMENTS						
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T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document						

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 30 4947

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 The members are as contained in the European Patent Office EDP file on
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18-10-2000

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
JP 05262987	A	12-10-1993	NONE		
EP 0545002	A	09-06-1993	JP 5140320 A JP 6040847 A JP 6040848 A US 5412004 A	08-06-1993 15-02-1994 15-02-1994 02-05-1995	
JP 02295912	A	06-12-1990	JP 2796990 B	10-09-1998	
US 5557000	A	17-09-1996	JP 7197055 A	01-08-1995	

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 For more details about this annex : see Official Journal of the European Patent Office, No. 12/82